USE OF SILOXANE-BASED POLYMERS OR COMPOSITES IN CHEMICAL SENSORS FOR DETECTING NITRO COMPOUNDS

DESCRIPTION

5   **TECHNICAL FIELD**

The present invention relates to the use of siloxane-based polymers or of composites comprising such a polymer and one or more electrically conductive fillers as sensitive materials in sensors for detecting

10   nitro compounds, and in particular nitroaromatic compounds such as nitrobenzene (NB), dinitrobenzene (DNB), trinitrobenzene (TNB), nitrotoluene (NT), dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT) and the like.

15   Such sensors are useful for detecting explosives, whether for the purpose of ensuring the safety of public places such as airports, for checking the legality of merchandise in circulation in a territory, for combating terrorism, for performing

20   disarmament operations, for locating antipersonnel mines or for decontaminating industrial or military sites.

They are also useful for environmental protection, in particular for controlling and

25   monitoring atmospheric pollution and the quality of more of less confined atmospheres, and also for the monitoring, for security purposes, of industrial sites that manufacture, store and/or handle nitro compounds.

PRIOR ART

The detection of explosives is a problem of vital importance, especially in terms of civil safety.

At the present time, several methods are used for detecting vapors of nitro compounds used in the preparation of explosives, for instance the use of sniffer dogs trained for this purpose, laboratory analysis, for example by chromatography coupled with a mass spectrometer or with an electronic trap detector, of samples collected on site, or alternatively infrared detection.

These methods generally show great sensitivity, which is fundamental in terms of detecting explosives, given the very low concentration of vapors of nitro compounds that prevails in the vicinity of an explosive. However, they are not entirely satisfactory.

Thus, the use of sniffer dogs has the drawback of requiring long training of the dogs and of their handlers, and of being unsuitable for prolonged operations due to the fact that the attention span of dogs is limited.

As regards the other methods, the physical bulk of the apparatus they use, their energy consumption and their operating costs run counter to the development of detection systems that are easily transportable and autonomous and, consequently, able to be used on sites of any type.

In recent years, the development of sensors capable of the real-time detection of gaseous chemical species is in full expansion. The functioning of these sensors is based on the use of a film of a sensitive

material, i.e. a material for which at least one physical property is modified on contact with the gaseous molecules sought, which amounts to a system capable of the real-time measurement of any variation of this physical property and thus of demonstrating the presence of the gaseous molecules sought.

The advantages of chemical sensors over the other abovementioned methods are manifold: immediacy of the results, possibility of miniaturization and therefore great portability, handleability and autonomy, low manufacturing and operating costs, etc.

However, it is obvious that their efficiency is extremely variable depending on the nature of the sensitive material used.

For the detection of gaseous nitro compounds, and more particularly of nitroaromatic compounds, many sensitive materials have already been proposed, among which mention may be made of porous silicon, plant charcoal, polyethylene glycol, amines, cyclodextrins, cavitands and fluorescent polymers (references [1] to [5]).

Moreover, the potential use of functionalized polysiloxanes as sensitive materials for sensors intended for detecting nitroaromatic compounds has been studied by McGill et al. (reference [6]).

These authors focused on determining the solubility parameters of a number of nitroaromatic compounds (NB, NT, TNB, DNT and TNT) and on defining, from these parameters, their sorption properties in the vapor state (i.e. their ability to be absorbed and

retained) in a series of polymers including various polysiloxanes.

McGill et *al.* deduce from the results they obtain that nitroaromatic compounds are capable of interacting with polymers proportionately more strongly when these polymers have solubility parameters that are complementary to those of said nitroaromatic compounds. They conclude therefrom that the most promising polysiloxanes for detecting nitroaromatic compounds are those whose monomers comprise an aromatic ring bearing one or more groups capable of establishing hydrogen bonds with these compounds, for example a hexafluoroisopropanol (HFIP) group. It is a fact that the DNT detection tests they perform using a sensor with surface waves equipped with a thin film of a polysiloxane derived from monomers containing an aromatic ring bearing an HFIP side group appear to give satisfactory results.

However, in the context of their studies on the development of sensors more especially intended for detecting explosives, the inventors have found that, entirely surprisingly, sensors using, as sensitive materials, siloxane-based polymers that comprise neither an aromatic ring nor a side group of HFIP type detect nitro compounds, and in particular nitroaromatic compounds, with a markedly higher sensitivity than sensors using the polysiloxanes recommended by McGill et *al.*

This finding is the basis of the invention.

DESCRIPTION OF THE INVENTION

One subject of the invention is the use of at least one polymer comprising at least one siloxane repeating unit corresponding to the general formula (I) below:

$$\left(\begin{array}{c} R_1 \\ | \\ X \\ | \\ -Si-O- \\ | \\ Y \\ | \\ R_2 \end{array}\right) \qquad (I)$$
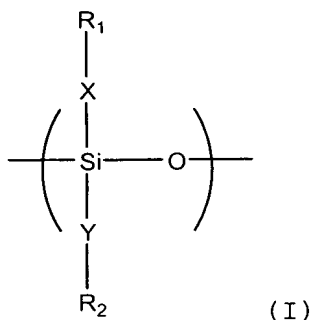
in which:

X and Y, which may be identical or different, represent a single bond or a saturated or unsaturated, linear hydrocarbon group containing from 1 to 50 carbon atoms;

R_1 and R_2, which may be identical or different, represent a hydrogen atom, a CN group, a group $C(Z)_3$, $CH(Z)_2$ or CH_2Z with Z representing a halogen atom; an NH_2 group, a group NHR_3 or NR_3R_4 with R_3 and R_4 representing, independently of each other, a halogen atom, a methyl group or a linear or branched, saturated or unsaturated hydrocarbon chain containing from 2 to 20 carbon atoms and possibly one or more heteroatoms and/or one or more chemical functions comprising at least one heteroatom; on condition, however, that at least one from among R_1 and R_2 is not a hydrogen atom; or of a composite comprising this polymer and one or more electrically conductive fillers, as sensitive

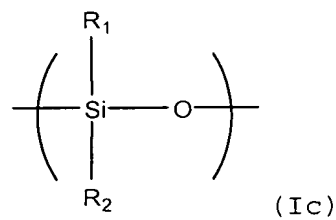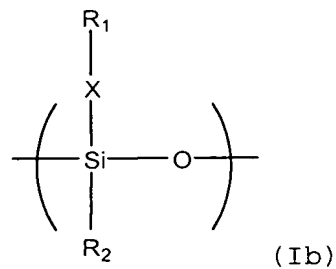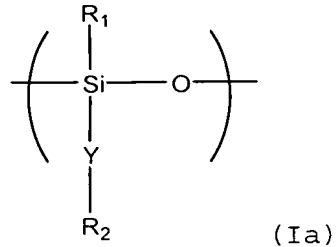material in a sensor for detecting one or more nitro compounds.

In the general formula (I) above, when R_3 and/or R_4 represent a C_2 to C_{20} hydrocarbon chain and when this chain comprises one or more heteroatoms and/or one or more chemical functions, then these atoms and these functions may either form a bridge within this chain or may be borne laterally thereby, or alternatively may be located at the end thereof.

The heteroatom(s) may be any atom other than a carbon or hydrogen atom, for instance an oxygen, sulfur, nitrogen, fluorine, chlorine, phosphorus, boron or silicon atom.

The chemical function(s) may be chosen especially from -COOH, -COOR$_5$, -CHO, -CO-, -OH, -OR$_5$, -SH, -SR$_5$, -SO$_2$R$_5$, -NH$_2$, -NHR$_5$, -NR$_5$R$_6$, -CONH$_2$, -CONHR$_5$, -CONR$_5$R$_6$, -C(Z)$_3$, -OC(Z)$_3$, -COZ, -CN, -COOCHO and -COOCOR$_5$ functions in which:

- R_5 represents a linear or branched, saturated or unsaturated hydrocarbon group containing from 1 to 100 carbon atoms, or a covalent bond when said chemical function(s) form(s) a bridge in a C_2 to C_{20} hydrocarbon chain;
- R_6 represents a linear or branched, saturated or unsaturated hydrocarbon group containing from 1 to 100 carbon atoms, this group possibly being identical to or different from the hydrocarbon group represented by R_5; while
- Z represents a halogen atom, for example a fluorine, chlorine or bromine atom.

Moreover, in the general formula (I), when X and/or Y represents a single bond, then R_1 and/or R_2 are respectively linked directly to the silicon atom via a covalent bond such that the siloxane repeating unit corresponds to one of the particular formulae (Ia), (Ib) and (Ic) below:

$$\left(-\underset{\underset{\underset{R_2}{|}}{\underset{Y}{|}}{\overset{\overset{R_1}{|}}{Si}}-O-\right) \quad \text{(Ia)}$$

$$\left(-\underset{\underset{R_2}{|}}{\overset{\overset{\overset{R_1}{|}}{X}}{Si}}-O-\right) \quad \text{(Ib)}$$

$$\left(-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{Si}}-O-\right) \quad \text{(Ic)}$$

in which X, Y, R_1 and R_2 have the same meaning as above.

According to one preferred arrangement of the invention, the siloxane repeating unit corresponds to the particular formula (Id) below:

$$\underset{CH_3}{\overset{R_1}{\overset{|}{\underset{|}{\overset{X}{\underset{|}{\left(\!\!\!-\!Si\!-\!O\!-\!\right)}}}}}}\quad (Id)$$
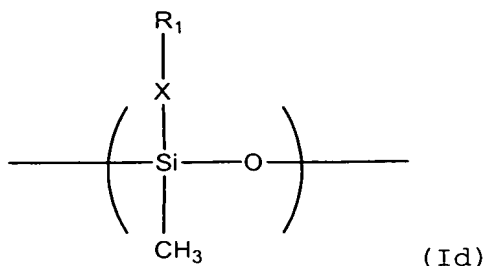
in which X is a saturated or unsaturated linear hydrocarbon group containing from 1 to 50 carbon atoms, while R_1 has the same meaning as above.

Among the siloxane repeating units of particular formula (Id) that are especially preferred are those in which X represents an alkylene chain containing from 2 to 10 carbon atoms (i.e. a chain $(CH_2)_n$ in which n ranges from 2 to 10) and, among these units, trifluoropropylmethylsiloxane (X = $(CH_2)_2$, $R_1 = CF_3$) and cyanopropylmethylsiloxane (X = $(CH_2)_3$, $R_1 = CN$).

According to another preferred arrangement of the invention, the polymer is a homopolymer, i.e. it consists of only one siloxane repeating unit of general formula (I), in which case it is advantageously chosen from polytrifluoropropylmethylsiloxanes and polycyano-propylmethylsiloxanes, and more particularly from those with an average molecular weight ranging from 50 to 100 000.

As a variant, the polymer may also be a copolymer, in which case it may either consist of different siloxane repeating units all corresponding to the general formula (I) or comprise one or more siloxane repeating units of general formula (I) and one

or more other, siloxane or non-siloxane, repeating units.

Specifically, it may be useful, for example, to include in the polymer repeating units

5   derived from a monomer of the type such as ethylene, propylene, ethylene oxide, styrene, vinylcarbazole or vinyl acetate, which are capable of giving it better mechanical strength especially when it is desired to use it in the form of a thin film.

10 Since the polymers containing a siloxane repeating unit of the general formula (I) are not intrinsically electrically conductive, it is possible, in accordance with the invention, to mix them with one or more conductive fillers in an amount that is

15 sufficient for the resulting composites to have an electrical conductivity suited to their use as sensitive materials of resistive sensors. These conductive fillers may be, for example, carbon black particles or metal (Cu, Pd, Au, Pt, etc.) or metal

20 oxide (V_2O_3, TiO, etc.) powders.

According to yet another preferred arrangement of the invention, the polymer or the composite is in the form of a thin film that covers one or both faces of a substrate suitably chosen as a

25 function of the physical property of the sensitive material whose variations are intended to be measured by this sensor.

As a variant, the polymer or the composite may also be in a bulk form, for instance a cylinder

30 having a certain porosity so as to make all of the

molecules forming said polymer or said composite available to the nitro compounds.

When it is in the form of a thin film, this film is preferably from 10 angstroms to 100 microns thick.

Such a film may be obtained via any of the techniques proposed to date for preparing a thin film on the surface of a substrate, for example:

- by spraying, by spin coating or by drop coating of a solution containing the polymer or the composite onto the substrate,
- by dip coating of the substrate in a solution containing the polymer or the composite,
- via the Langmuir-Blodgett technique,
- by electroplating, or
- by polymerization *in situ*, i.e. directly onto the surface of the substrate, of a precursor monomer of the polymer.

The substrate and the measuring system of the sensor are chosen as a function of the physical property of the polymer or of the composite whose variations induced by the presence of nitro compounds are intended to be measured by the sensor.

In the present case, the variations of two physical properties proved to be particularly advantageous to measure: the variations in mass in the case of a polymer and the variations in electrical conductivity in the case of a composite.

Thus, the sensor is preferably a gravimetric sensor for measuring variations in mass, or

a resistive sensor for measuring variations in electrical conductivity.

Examples of gravimetric sensors that may be mentioned include sensors of the quartz microbalance type, surface acoustic wave (SAW) sensors, such as Love wave sensors and Lamb wave sensors, and also microlevers.

Among the gravimetric sensors that are more particularly preferred are sensors of the quartz microbalance type. This type of sensor, the operating principle of which is described in reference [2], comprises, schematically, a piezoelectric substrate (or resonator), generally a quartz crystal covered on its two faces with a layer of metal, for example of gold or platinum, and which is connected to two electrodes. Since the sensitive material covers one or both faces of the substrate, any variation in the mass of this material is reflected by a variation in the vibration frequency of the substrate.

Needless to say, it is also possible to use a polymer or a composite as defined previously, as sensitive material in sensors designed to measure variations in a physical property other than the mass and the electrical conductivity, for instance variations in an optical property such as fluorescence, luminescence, absorbance in the UV-visible range or wavelength in the infrared range.

In this case, it is possible either to exploit an intrinsic optical property of the polymer or of the composite when it has one (absorbance, IR spectrum, etc.) or to give this polymer or this

composite a particular optical property by coupling with a suitable marker, for example a fluorescent or luminescent marker.

Moreover, it is also possible to combine within the same device or "multisensor" several sensors comprising sensitive materials that are different from each other, or equipped with substrates and measuring systems that are different from each other, for instance one or more gravimetric sensors and/or one or more resistive sensors, the essential being that at least one of these sensors comprises a polymer or a composite as defined above.

According to yet another preferred arrangement of the invention, the nitro compound(s) intended to be detected by the sensor is(are) chosen from nitroaromatic compounds, nitroamines, nitrosamines and nitric esters, these compounds possibly being in solid, liquid or gaseous (vapors) form.

Examples of nitroaromatic compounds that may be mentioned include nitrobenzene, dinitrobenzene, trinitrobenzene, nitrotoluene, dinitrotoluene, tri-nitrotoluene, dinitrofluorobenzene, dinitrotrifluoro-methoxybenzene, aminodinitrotoluene, dinitrotrifluoro-methylbenzene, chlorodinitrotrifluoromethylbenzene, hexanitrostilbene, trinitrophenylmethylnitramine (or tetryl) or trinitrophenol (or picric acid).

Examples of nitramines include cyclotetramethylenetetranitramine (or octogen), cyclo-trimethylenetrinitramine (or hexogen) and tetryl, while an example of a nitrosamine is nitrosodimethylamine.

As regards the nitric esters, they are, for example, pentrite, ethylene glycol dinitrate, diethylene glycol dinitrate, nitroglycerine or nitro-guanidine.

5   Sensors comprising a polymer or a composite as defined above, as sensitive material, have been found to have many advantages, especially:

- an ability to detect nitro compounds, and in particular nitroaromatic compounds, with very high
10   sensitivity since they are capable of detecting their presence at concentrations of the ppm (part per million) order, or even of the tenth of a ppm order,

- rapid response and reproducibility of this
15   response,

- ability to function continuously,

- stability of the performance over time,

- very satisfactory service life,

- manufacturing cost compatible with a production of
20   sensors in series, a very small amount of polymer or of composite (i.e., in practice a few mg) being necessary for the manufacture of a sensor, and

- possibility of being miniaturized and, consequently, of being easily transportable and
25   handleable on all types of sites.

They are therefore particularly useful for detecting explosives, especially in public places.

Other characteristics and advantages of the invention will emerge more clearly on reading the
30   additional description that follows, which relates to examples of using thin films of

polytrifluoropropylmethylsiloxane   and   of
polycyanopropylmethylsiloxane   in   quartz   microbalance
sensors   for   the   detection   of
dinitrotrifluoromethoxybenzene   (DNTFMB)   and

5   dinitrobenzene (DNB) vapors, and which refers to the
attached drawings.

The choice of DNTFMB and of DNB as nitro
compounds to be detected was driven by the fact that
these compounds are very similar to dinitrotoluene

10   (DNT), which is the nitro derivative most commonly
present in the chemical signature of mines based on
trinitrotoluene (TNT).

Needless to say, the examples that follow
are given merely as illustrations of the subject of the

15   invention and do not in any way constitute a limitation
of this subject.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents the change in the
vibration frequency (curve A) of the quartz of a quartz

20   microbalance   sensor   comprising   a   thin   film   of
polytrifluoropropylmethylsiloxane in the course of two
cycles of exposure (curve B) of this sensor to DNTFMB
vapors at a concentration equal to 3 ppm.

Figure 2 represents the change in the

25   vibration frequency (curve A) of the quartz of a quartz
microbalance   sensor   comprising   a   thin   film   of
polytrifluoropropylmethylsiloxane in the course of two
cycles of exposure (curve B) of this sensor to DNB
vapors at a concentration equal to 150 ppb (parts per

30   billion).

Figure 3 represents the change in the vibration frequency (curve A) of the quartz of a quartz microbalance sensor comprising a thin film of polycyanopropylmethylsiloxane in the course of a cycle

5   of exposure (curve B) of this sensor to DNTFMB vapors at a concentration equal to 3 ppm.

Figure 4 represents the change in the vibration frequency (curve A) of the quartz of a quartz microbalance sensor comprising a thin film of

10   polycyanopropylmethylsiloxane in the course of two cycles of exposure (curve B) of this sensor to DNTFMB vapors at a concentration equal to 1 ppm for the first cycle and 0.1 ppm for the second.

Figure 5 represents the values of the

15   variations in the vibration frequency (ΔF) of the quartz of a quartz microbalance sensor comprising a thin film of polycyanopropylmethylsiloxane as obtained by subjecting this sensor to twelve exposures to DNTFMB vapors for 10 minutes each, over a period of 150 days.

20   **EXAMPLES**

Example 1: Detection of DNTFMB by a sensor comprising a Thin film of polytrifluoropropylmethylsiloxane

In this example, a quartz microbalance sensor is used, comprising a quartz of cross section

25   AT, with a vibration frequency of 9 MHz, covered with two circular gold measuring electrodes (model QA9RA-50, Ametek Precision Instruments) and bearing on its two faces a thin film of polytrifluoropropylmethylsiloxane.

This film is deposited by spraying a

30   solution of polytrifluoropropylmethylsiloxane (from the

company ABCR, reference FMS-9921) in chloroform, with a concentration equal to 5 g/l, 6 times for 0.5 seconds each onto each face of the quartz.

5   The variation in the vibration frequency of the quartz due to this deposition is 8.1 kHz.

The sensor is subjected to two cycles of exposure to DNTFMB vapors, at room temperature:

- the first cycle comprising a phase of exposure to ambient air for 5800 seconds, followed by a phase of
10   exposure to the DNTFMB vapors for 600 seconds, and then a phase of exposure to ambient air for 2600 seconds;

- the second cycle comprising a phase of exposure to DNTFMB vapors for 600 seconds, followed by a phase of exposure to ambient air for 4800 seconds;
15   the DNTFMB concentration being 3 ppm in the two cycles.

Figure 1 shows the change in the vibration frequency of the quartz in the course of these two cycles, curve A and curve B corresponding to the respective variations of said frequency (F), expressed in hertz (Hz), and of the concentration of DNTFMB
20   ([C]), expressed in ppm, as a function of the time (t), expressed in seconds.

Example 2: Detection of DNB with a sensor comprising a
25   **Thin film of polytrifluoropropylmethylsiloxane**

In this example, a quartz microbalance sensor is used comprising a quartz identical to that used in Example 1, but in which the quartz is covered on both faces with a thin film of polytrifluoro-
30   propylmethylsiloxane slightly thicker than that used in Example 1.

This film is deposited by spraying a solution of polytrifluoropropylmethylsiloxane in chloroform, with a concentration equal to 2 g/l, 19 times for 0.2 second each onto each face of the quartz.

5   The variation in the vibration frequency of the quartz due to this deposit is 9.9 kHz.

The sensor is subjected to two cycles of exposure to DNB vapors, at room temperature:

- the first cycle comprising a phase of exposure

10   to ambient air for 1700 seconds, followed by a phase of exposure to the DNB vapors for 600 seconds, and then a phase of exposure to ambient air for 2300 seconds;

- the second cycle comprising a phase of exposure to DNB vapors for 600 seconds, followed by a phase of

15   exposure to ambient air for 1800 seconds;
the DNB concentration being 150 ppb in the two cycles.

Figure 2 shows the change in the vibration frequency of the quartz in the course of these two cycles, curve A and curve B corresponding to the

20   respective variations in said frequency (F), expressed in Hz, and in the DNB concentration ([C]), expressed in ppb, as a function of time (t), expressed in seconds.

Example 3: Detection of DNTFMB with a sensor comprising

25   **a thin film of polycyanopropylmethylsiloxane**

In this example, a quartz microbalance sensor is used comprising a quartz identical to that used in Example 1, but in which the quartz is covered on both faces with a thin film of polycyanopropyl-

30   methylsiloxane.

This film is deposited by spraying a solution of polycyanopropylmethylsiloxane (from the company ABCR, reference YMS-T31) in chloroform, with a concentration equal to 5 g/l, 12 times for 0.2 second each onto each face of the quartz.

The variation in the vibration frequency of the quartz due to this deposit is 8.5 kHz.

The sensor is subjected to a cycle of exposure to DNTFMB vapors with a concentration equal to 3 ppm, at room temperature, this cycle comprising a phase of exposure to ambient air for 3000 seconds, followed by a phase of exposure to DNTFMB vapors for 600 seconds, and then a phase of exposure to ambient air for 11400 seconds.

Figure 3 shows the change in the vibration frequency of the quartz during this cycle, curve A and curve B corresponding to the respective variations in said frequency (F), expressed in Hz, and in the DNTFMB concentration ([C]), expressed in ppm, as a function of time (t), expressed in seconds.

Example 4: Detection of DNTFMB by a sensor comprising a thin film of polycyanopropylmethylsiloxane

In this example, a quartz microbalance sensor is used comprising a quartz identical to that used in Example 1, but in which the quartz is covered on both faces with a thin film of polycyanopropyl-methylsiloxane.

This film is deposited by spraying a solution of polycyanopropylmethylsiloxane (from the company ABCR, reference YMS-T31) in chloroform, with a

concentration equal to 5 g/l, twice for 0.5 second each onto each face of the quartz.

The variation in the vibration frequency of the quartz due to this deposit is 2 kHz.

The sensor is subjected to two cycles of exposure to DNTFMB in the form of vapors, at room temperature:

- the first cycle comprising a phase of exposure to ambient air for 1300 seconds, followed by a phase of exposure to DNTFMB at a concentration of 1 ppm for 600 seconds, and then a phase of exposure to ambient air for 6400 seconds;

- the second cycle comprising a phase of exposure to DNTFMB at a concentration of 0.1 ppm for 600 seconds, followed by a phase of exposure to ambient air for 1100 seconds.

Figure 4 shows the change in the vibration frequency of the quartz during these cycles, curve A and curve B corresponding to the respective variations in said frequency (F), expressed in hertz (Hz), and in the DNTFMB concentration ([C]), expressed in ppm, as a function of time (t), expressed in seconds.

Example 5: Study of the stability over time of the performance of a sensor comprising a thin film of polycyanopropylmethylsiloxane

In this example, a quartz microbalance sensor equal to that used in Example 4 is used.

This sensor is subjected to a first exposure to DNTFMB vapors at a concentration equal to

3 ppm, at room temperature for 10 minutes, and it is then stored in ambient air.

It is then subjected to eleven other exposures to DNTFMB vapors at a concentration equal to 3 ppm, still at room temperature and for a duration of 10 minutes each, spread over a period of 150 days.

Figure 5 represents the values of the variations in the vibration frequency (ΔF) of the quartz observed during these twelve exposures, these values being determined for each exposure as follows:

ΔF = vibration frequency at time t_0 of the exposure – vibration frequency at time t_{10min} of the exposure,

and symbolized by diamonds on said Figure 5.

Example 6: Comparison of the performance of a sensor comprising a thin film of a polysiloxane that is useful according to the invention and of a sensor comprising a thin film of a polysiloxane recommended by McGill et al.

In this example, two quartz microbalance sensors are used both comprising a quartz identical to that used in Example 1, but differing from each other in that the quartz of the first is coated on both faces with a thin film of polycyanopropylmethylsiloxane, whereas the quartz of the second is coated with a thin film of a polysiloxane whose monomers comprise an aromatic ring and two HFIP side groups.

This polysiloxane corresponds to formula (II) below:

$$m = 47, n = 53$$
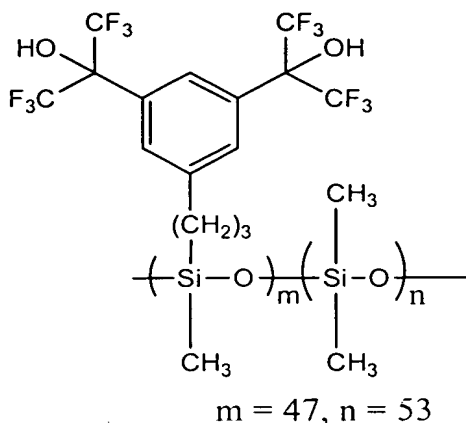
The films are deposited such that the variation in the vibration frequency of the quartzes due to these deposits is equal to 2 kHz for each of the sensors.

To do this, the polycyanopropylmethylsiloxane film is deposited as described in Example 4, whereas the film of the polysiloxane of formula (II) is deposited by spraying a solution of said polysiloxane in dichloromethane, with a concentration equal to 2 g/l, 6 times for 0.2 second onto both faces of the quartz.

The two sensors are exposed, under exactly the same conditions, to DNTFMB vapors at a concentration equal to 3 ppm, at room temperature for 10 minutes.

The measurement of the vibration frequency of the quartz of the two sensors at time t_0 and at time t_{10min} of this exposure gives a variation in the vibration frequency of 600 Hz for the quartz of the sensor comprising the thin film of polycyanopropylmethylsiloxane, and of 200 Hz - i.e. 3 times smaller -

for the quartz of the sensor comprising the thin film of the polysiloxane of formula (II).

Examples 1 to 4 above show that sensors comprising a sensitive material in accordance with the invention are capable of detecting with very great sensitivity nitro compounds such as DNTFMB and DNB. They also show that the response of these sensors is both reversible and reproducible.

Example 5 furthermore shows that the performance of these sensors is stable over time and that they are still capable, five months after their production, of detecting very small amounts of DNTFMB.

Finally, Example 6 shows that these sensors have, with regard to nitroaromatic compounds, very markedly higher sensitivity than that of a sensor comprising a thin film of a polysiloxane as recommended by McGill et *al*.

CITED REFERENCES

[1] Content et *al.*, *Chem. Eur. J.*, <u>6</u>, 2205, 2000

[2] Sanchez-Pedrono et *al.*, *Anal. Chim. Acta*, <u>182</u>, 285, 1986

[3] Yang et *al.*, *Langmuir*, <u>14</u>, 1505, 1998

[4] Nelli et *al.*, *Sens. Actuators B*, <u>13-14</u>, 302, 1993

[5] Yang et *al.*, *J. Am. Chem. Soc.*, <u>120</u>, 11864, 1998

[6] McGill et *al.*, *Sensors and Actuators B65*, 5-9, 2000